Chapter 10
Biomass Pretreatments for Biorefinery Applications: Gasification

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Abstract Biorefinery is the object of significant research and development efforts due to the scarcity of economically viable crude oil, renewable energy source, and its environmental benefits. This has prompted chemical corpo-rations to look for alternative sources of carbon and hydrogen to produce chemicals, biologics, and other products such as biomass and waste matter. Two main reaction pathways are currently explored for biorefinery: thermochemical and biochemical. The thermochemical pathway proposes significantly higher reaction rates compared to current biological processes that use non-genetically modified organisms. One of the thermochemical pathways for biomass conversion is gasification which is a decomposition of solid fuels at high temperatures and oxygen-lean atmosphere. The successful development of biomass gasification processes requires addressing several critical technical difficulties including biomass diversity, feedstock treatment, gasification mechanism and reactions, gasifier types, and their performances. This chapter reviews key features of biomass gasification as a pretreatment for biorefining which can be used as a practical guide for gasification process. This chapter consists of six sections that include types of biomass for gasification, their properties, and pretreatment steps; gasification mechanism and reactions; syngas cleaning and conditioning; different gasifier, their characteristics, and modeling.

Keywords Biomass gasification · Pretreatment · Gasifier · Gas cleaning · Tar removal · Catalytic gasification

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10.1 Introduction

The beginning of industrial civilization has triggered the frantic use of non-renewable fossil-fuel resources (coal first, followed by oil and gas), which has grown worldwide ever since. Today, the price of fossil fuels is increasing due to depleting "conventional" resources, rising demands from developing countries and the establishment of a low-carbon economy. In this context, significant investments and research are focusing on the development of new processes to extract energy and goods from renewable resources, such as biomass.

Biomass is a carbonaceous matter, known as a renewable energy source from living or recently living organisms. Examples include forest residue, agricultural wastes, and even, municipal solid waste. To convert biomass, two main reaction pathways are currently considered: biochemical and thermochemical. Gasification is a thermo-chemical pathway, which transfers the combustion value of the solid fuel to the gas phase whose composition maximizes its chemical energy rather than sensible heat. Syngas, a mixture of CO and H_2, is one of the products of the gasification process, which could be used as a fuel or building block for many hydrocarbons. The products derived from syngas can be divided into three categories: (1) chemicals, such as ammonia and methanol; (2) transportation fuels, such as synthetic natural gas and synthetic diesel; (3) and energy feedstock, such as methane. Currently, syngas is produced mainly from fossil fuels; however, there is a growing interest in generating "green chemicals" and "green fuels" from the gasification process.

To successfully design an industrial gasification process, a thorough knowledge of biomass pretreatment, gasification reaction kinetics, and reactor technologies is essential. This chapter discusses the subject of biomass gasification through a detailed review of the scientific and industrial literature.

10.2 Types of Biomass for Gasification

The biomass properties have significant effects on the product compositions (through conservation of mass) and the gasification conditions (corrosion, slagging, etc.). Biomass includes any form of non-fossilized and biodegradable material derived from living species, such as plants and animals. The term "biomass" designates a very wide spectrum of substances, which includes products, byproducts, residues, and wastes from industries (forestry, agricultural, food, etc.) and municipalities [1, 2]. Each type of biomass is characterized by its specific physical and chemical properties: moisture, heating value, bulk density, chemical composition as well as ash and volatile contents. The biomass properties determine its performance as a fuel in gasification or any other process. Furthermore, the availability of the types of biomass as well as their properties is a function of a geographical location.

One of the most available biomass is wood, but it is a valuable material due to its current applications as a construction material. Wood residues (sawdust, bark, and misshapen pieces), however, have very little market value and are therefore prime candidates to be used as gasification feedstock. Other types of industrial residues (agricultural, forestry, etc.) could also be used as feedstock: husks from rice, coffee or coconut, bagasse from sugar cane, and verge grass. Energy cropping, such as poplar, sugar cane, and sweet sorghum, which consists of growing biomass specifically for fuels, is also another interesting possibility in renewable energy and the agricultural sector.

10.2.1 Biomass Properties

One important aspect of biomass is its potential for carbon offsetting. The energy conversion of biomass does not contribute to CO_2 emission or global warming. CO_2 released during biomass conversion is equivalent to the quantity it absorbed during its growth. In other words, energy production from biomass is almost carbon neutral. The veracity of this statement is, however, debatable as the calculation of the carbon balance associated with biomass conversion is complex: Many parameters must be considered, such as growth, harvest, transportation, and pretreatments. Yet the use of biomass fuels can result in the displacement of carbon dioxide emissions that are ordinarily released when using fossil fuels. *This displacement will depend entirely on the efficiency with which the biomass energy can be produced and used.*

Most biomass materials contain very low amounts of sulfur, chlorine, in comparison to most fossil fuels. Biomass conversion or its use as energy has the potential to lower pollutant emissions.

Biomass chemical composition is obtained through ultimate (also called elemental) and proximate analysis. Ultimate analysis yields the composition of biomass in terms of carbon, hydrogen, nitrogen, oxygen, and sulfur content (mass %). On the other hand, proximate analysis reports the composition in terms of volatile matter, ash, moisture, and fixed carbon. There are separate ASTM standards for measurements of individual components of biomass, such as volatile matter, ash, moisture, and fixed carbon.

- *Volatile matter* refers to the condensable and non-condensable vapor released during the early stages of biomass heating. It depends strongly on the heating rate and final temperature. There are different ASTM standards for the measurement of volatile matter; each standard is specific to different types of biomass.
- *Ash* is the inorganic residue composed mainly of silica, iron, calcium, magnesium, sodium, and sometimes potassium. It is the remaining material once biomass has been completely consumed in the reactor.
- *Fixed carbon* is an important parameter in biomass gasification, because its conversion is a limiting reaction, and it is used to size the gasifier.
- The *heating value* of the biomass is the energy chemically bound in the biomass with respect to a reference state. The best common ones are the lower heating value (LHV) where the reference state is water in its gas state and the higher heating value (HHV) where the reference state is water in its liquid state.

The biomass properties detailed above have significant effects on gasification conditions and product compositions: The basis on which they are measured and reported (wet, dry, or dry-ash-free basis) is very important. For example, low ash content improves thermal balance and reduces operating problems due to slagging and sintering. Water vapor is also an essential key component in gasification reactions; at high levels, it may negatively affect the process thermal balance. Biomass-containing sulfur, chlorine (may be present in low amounts), and alkali metals can also lead to the formation of corrosive components. Most biomass also contains nitrogen that can form gas-phase ammonia, which can oxidize and form NO_x.

10.2.2 Feedstock Pretreatments for Gasification

Pretreatment of the biomass feedstock is the first step in the gasification process. It is essential in some cases due to the process characteristics, but it generally helps to improve the quality of the fuel by homogenizing its size, moisture content, and density. For the operation of continuous processes, biomass storage is required, yet it may lead to issues related to decomposition and self-heating. Pretreatment can help solve or minimize the impact of these issues. It includes several processes, such as size reduction (milling, grinding, and pulverization), screening, drying, torrefaction, pelletization, and pyrolysis.

10.2.2.1 Drying and Size Reduction

The biomass feedstock moisture and ash content have an effect on the gasification product composition, the process energy balance, and the reactor operating condition. Different gasification processes require different moisture levels; high moisture content in biomass will, however, reduce the gasifier temperature and have negative effects on gasification efficiency and the quality of the products. To reduce moisture, driers are used and the most common type is the rotary drier. Nevertheless, the use of steam drying techniques is also increasing due to its easy integration into existing systems. Other techniques, such as biomass mechanical dewatering and leaching with water, have been demonstrated to reduce ash content efficiently [3]. Since water vapor plays an essential role in the chemical reactions of the gasification process, there is a trade-off between moisture removal (beneficial to the process energy balance) and syngas composition.

Biomass particle-size reduction techniques include milling, grinding, and pulverization, which make drying, transfer, and biomass storage easier. Their use depends mainly on the requirements of the gasification system as well as the biomass characteristics. For example, to pulverize particles to an average size below 0.2 mm, a vibration mill is recommended [4]. There are also some new methods being developed, like freezing pulverization or explosion disintegration, which are suitable for materials that could not be pulverized by conventional methods; however, their power consumption is relatively high.

10.2.2.2 Torrefaction

Torrefaction is a biomass thermal treatment process at low temperature (200–300 °C) in the absence of oxygen and mostly at near atmospheric pressure. It is a mild pyrolysis process that destroys the fibrous structure of biomass, increasing its calorific value as well as its hydrophobic nature to improve biomass stability during storage. Since torrefied biomass is more friable compared to its original state, energy consumption for biomass particle-size reduction is lower. It has also been shown that torrefied biomass particles can be fluidized more smoothly compared to untreated biomass [5]. There are two main torrefaction methods: (1) the wet process [6] and (2) the dry process. In wet torrefaction, biomass is treated with hot compressed water resulting in three groups of products: solid fuel, aqueous compounds, and gases. Dry torrefaction is an intensive drying at higher temperatures [7]. One of the drawbacks of the wet process is the necessity to separate the excess water from the torrefied biomass and liquid by-products with relatively high organic and mineral contents. Dry torrefaction is typically performed at temperatures in the range of 230–300 °C in the absence of oxygen, at near atmospheric pressure and a relatively low particle heating rate (lower than 50 °C/min). The mass and energy yield from the original biomass to the torrefied biomass is strongly dependent on torrefaction temperature, reaction time, and biomass type.

10.2.2.3 Pyrolysis

Biomass offers some advantages as a feedstock due to its high volatile content and high char reactivity. Compared to fossil fuels, however, biomass is a solid with a low heating value, containing much less carbon and more oxygen. In general, it is important to remove oxygen when producing fuel from biomass because high oxygen content results in low energy density. Biomass contains about 40–60 wt % oxygen compared to less than 1 wt % for fossil fuel. Pyrolysis can be used as a pretreatment process to reduce the oxygen content in biomass to lower levels compared to torrefaction depending on the operating condition.

Biomass pyrolysis yields three products: semi-char solid, liquid bio-oil (condensable gases), and a non-condensable gaseous fraction. The non-condensable gaseous fraction is composed mainly of hydrogen, carbon dioxide, carbon monoxide, and methane. Following the biomass feedstock pyrolysis, the solid and liquid products of pyrolysis can be mixed and fed as slurry to the gasifier, which is advantageous for entrained bed reactors [8]. However, bio-oils mainly contain double carbon bound chemicals. These materials tend to polymerize and become increasingly viscous, which is detrimental to its stability during storage.

It is also important to note that the pyrolysis conditions have an effect on the reactivity of the char produced during gasification. Therefore, the proper selection of pyrolysis conditions is the key to ensure the gasification process will benefit [9].

As discussed in this section, there are several methods for biomass pretreatment, which can be combined for the benefit of the gasification process. Each method has its specific advantages as well as disadvantages, and the best selection depends on the feeder characteristics and gasifier type.

10.3 Biomass Gasification

Gasification is the conversion of solid fuels into gas fuels in an *oxygen-lean atmosphere.* Pyrolysis, gasification, and combustion are classified as three separate thermo-chemical conversion processes. However, both pyrolysis and combustion take place during gasification. In gasification, at least four different stages of reactions are involved: (1) pyrolysis, (2) combustion of solid char and other gases, (3) gasification of char, and (4) tar cracking.

Different types of gasifiers must deal with these reactions. The contribution of these reactions upon the final gaseous product as well as the specific conversion of each reaction depends on the operating conditions (temperature, pressure, etc.), the biomass characteristics (chemical composition, particle size, etc.), and gasifier type. The fundamental gasification reactions (reduction reactions) are endothermic. The necessary energy is supplied by the exothermic combustion reactions. Compared to the original solid fuel, the produced gaseous fuel is easy to clean, to transport, and if cleaned properly it can be used in fuel cells as well as burned in gas turbines, furnaces, boilers, and reciprocating engines [10].

As mentioned earlier, syngas is one of the products of gasification, which is an important source for valuable chemicals and energy, such as hydrogen, diesel (through Fischer–Tropsh synthesis), electricity (through combustion), fertilizer (through ammonia production), and methanol.

In the gasification process, heavier hydrocarbons, called tar, are produced along with syngas. Tar consists of high-molecular weight components, usually rich poly aromatic hydrocarbons (PAH). The presence of tar in syngas can cause serious problems in syngas applications. Condensation, fouling, and the polymerization of tar are general problems that can arise. The amount of undesirable products in the gas depends mainly on the design of the gasifier, feedstock characteristics as well as the gasifier operating conditions. Once the raw syngas leaves the gasifier, it goes through treatment processes, such as *gas cleaning* of dust or particulates (by cyclone, fabric or electrostatic filters, or solvent scrubber), *conditioning* (with the use of shift reaction to adjust the molar ratio of CO and H_2), and *separation* (to refine the syngas stream from tar and other catalyst poisons).

10.3.1 Reaction Kinetics

A good understanding of the gasification reaction kinetics and gasifier hydrodynamics is essential for the design, operation, and optimization of gasification processes. This section will discuss the main chemical reactions that govern gasification and the different kinetic models in the scientific literature that are available.

During a gasification process, the biomass particles undergo the following reaction steps:

1. Drying: The biomass particles are heated and dried on entering the reactor (endothermic step).
2. Pyrolysis (thermal cracking): As they reach high temperatures, the biomass particles undergo pyrolysis and decompose to gas and solid char (endothermic step).
3. Gasification:
    a. Combustion: The char and gases (condensable and non-condensable) react with oxygen to produce H_2O, CO, CO_2 (exothermic step).
    b. Gasification: Where the produced gas and solid char from previous steps react with the gasifying agent and each other (endothermic step).
    c. Tar cracking: The condensable gas decomposes (thermal cracking) to smaller molecular weight components (endothermic).

The level of oxygen in the gas can be set in order for the system to be autothermal. These steps are generally modeled in series, but it is widely accepted that there are no sharp boundaries between them. Table 10.1 lists the important reactions taking place during gasification.

10.3.1.1 Pyrolysis Kinetic

Pyrolysis is the cracking of hydrocarbon molecules into smaller gas molecules without any major reaction with air or any other gasifying medium. The kinetic information of pyrolysis is crucial for the design and scale-up of any gasification process. Extensive investigations have been done on the kinetics of biomass devolatilization in an inert atmosphere. Table 10.2 shows the most widely used kinetic schemes of biomass pyrolysis.

Earlier kinetic models consisted of simple, single first-order reaction schemes to describe the total volatile yield. Later, more complicated two- and three-step reaction networks containing parallel and series reactions were introduced by different authors [22, 24]. These are empirical models whose parameters are calculated by fitting experimental data generally derived from thermo-gravimetric measurements. Since most of the biomass is composed of cellulose, hemi-cellulose, and lignin, the most accurate models are reported to be a three independent parallel reactions model [25–29].

Most modeling efforts with the three independent parallel reactions model have been conducted using experimental data from a single heating rate [25, 30–33]. The effect of heating rate on the pyrolysis yield is, however, significant because the kinetic parameters derived from a single heating rate cannot be confidently extrapolated to other heating rates. Radmanesh and Chaouki proposed an improved model for biomass pyrolysis, which is applicable to different heating rates [27]. The kinetic parameters were calculated from experimental data obtained at relatively low heating rates (maximum heating rate was 50 ° C/min). Therefore the extrapolation of these kinetic models to actual gasification process conditions yields significant

Table 10.1 Gasification reactions

Reaction		Reference
Carbon reactions		
Boudouard	$C + CO_2 \rightarrow 2CO + 172\ kJ/mol$	[11]
Water–gas	$C + H_2O \rightarrow CO + H_2 + 131\ kJ/mol$	[12]
Hydro-gasification	$C + 2H_2 \leftrightarrow CH_4 - 74.8\ kJ/mol$	
	$C + \frac{1}{2}O_2 \rightarrow CO - 111\ kJ/mol$	[13]
Oxidation reactions		
	$2\left(\frac{\eta+1}{\eta+2}\right)C + O_2 \rightarrow \frac{2\eta}{\eta+2}CO + \frac{2}{\eta+2}CO_2$	[13]
	$CO + \frac{1}{2}O_2 \rightarrow CO_2 - 284\ kJ/mol$	[14]
	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O - 803\ kJ/mol$	[14]
	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O - 242\ kJ/mol$	[15]
Shift reaction	$CO + H_2O \leftrightarrow CO_{2+}H_2 - 41.2\ kJ/mol$	[16]
Methanation reaction		
	$2CO + 2H_2 \rightarrow CH_4 + CO_2 - 247\ kJ/mol$	
	$CO + 3H_2 \rightarrow CH_4 + H_2O - 206\ kJ/mol$	
	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O - 165\ kJ/mol$	
Steam reforming reactions		
	$CH_4 + H_2O \leftrightarrow CO + 3H_2 + 206\ kJ/mol$	
	$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2 - 36\ kJ/mol$	
Tar reactions		
Tar cracking	$tar\ (gas) \rightarrow \vartheta_{H_2}H_2\ (g) + \vartheta_{CH_4}CH_4\ (g)$ $+ \vartheta_{CO}CO\ (gas)$ $+ \vartheta_{CO_2}CO_2\ (gas)$ $+ \vartheta_{tar}tar_{inert}$	[17]
Tar combustion	$CH_{1.522}O_{0.0228} + 0.867O_2 \rightarrow CO + 0.761H_2O$	[18]

uncertainties since, in reality, biomass temperature increases very rapidly from ambient temperature to about 800–1,000 ° C (in less than 1 s) as it is fed into the gasifier [27]. Consequently, the actual heating rates applied to biomass particles in pyrolysis systems are significantly higher than 50 ° C/min or even 100 °C/min.

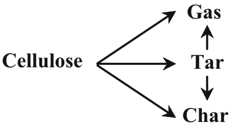
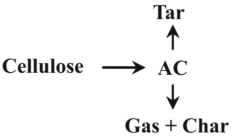
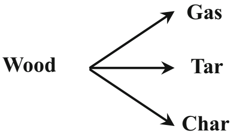
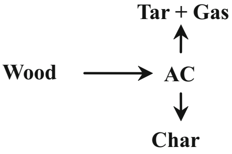
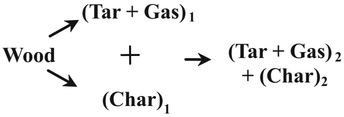
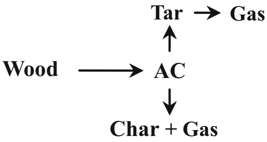
There are only a few studies on pyrolysis at high heating rates (1,000 °C/s) and the resulting gas production [34–37]. Although it is very important to have knowledge about pyrolysis kinetic gasification design and optimization, it is very difficult to obtain reliable data for kinetic constants that can be used for a wide range of biomass at different heating rates. Most models are derived from cellulose pyrolysis experiments, and the available models in the literature are only applicable to specific conditions.

10.3.1.2 Gasification Reaction Kinetics

In the gasification step that follows pyrolysis, several parallel reactions occur:

- *Char gasification* involves the reaction between char and steam, carbon dioxide, hydrogen, and oxygen (R1, R2, R3, and R4 shown in Table 10.1). These reactions

Table 10.2 Summary of the proposed kinetics for biomass pyrolysis

	Biomass type	Kinetic scheme	Ref.
1	Cellulose		[19]
2	Cellulose		[20]
3	Wood		[21]
4	Wood		[22]
5	Wood	 (Tar + Gas)₁ Wood + (Tar + Gas)₂ + (Char)₂ (Char)₁	[23]
6	Cellulose		[24]

are endothermic, except for those involving O_2 and H_2 which are exothermic. The rate of these reactions depends on the reactivity of char and the gasifying medium: Oxygen is the most reactive species followed by steam and carbon dioxide. Char oxidation reactions are so fast that most of the oxygen is used in this specific reaction step. The relative reaction rates of the gasification reactions are estimated by Walker et al. [38]:

$$R_{\mathrm{C+O_2}} \gg R_{\mathrm{C+H_2O}} \gg R_{\mathrm{C+CO_2}} \gg R_{\mathrm{C+H_2}}$$

- Char is usually assumed to be pure carbon for simplification. In reality, it is composed of small amounts of hydrocarbon. Biomass char is generally more porous and reactive compared to coal char, so its reaction should be considered different [39].

- Water–gas (R2) reaction involves hydrogen, which affects char and steam reaction negatively as shown by Barrio et al. [40]. The continuous removal of hydrogen from the reactor is necessary in order to accelerate water–gas reactions.
- The gasification of char with carbon dioxide (known as Boudouard reaction—R1) is a relatively slow reaction. The rate of this reaction is negligible below 1,000k [41].
- Water–gas shift reaction (R8) is an important kinetic step in the gas phase. It controls the production and the ratio of hydrogen and carbon monoxide, which is critical for downstream processes. It is a slightly exothermic equilibrium reaction with negligible sensitivity to pressure. Above 1,000 °C, it reaches equilibrium fast but a heterogeneous catalyst is required to reach equilibrium at lower temperatures. Probstein and Hicks showed that at lower temperatures the reaction has a higher equilibrium constant, which means a higher hydrogen yield with low reaction rates [42]. Different catalysts have been tested and employed for water–gas shift reaction, like copper promoted catalysts for the temperature range of 300–510 °C, and a copper–zinc–aluminum oxide catalyst for the 180–270 °C range in commercial applications [43].
- As mentioned before, one of the products of gasification is a condensable heavy hydrocarbon, known as tar. Produced tar from the pyrolysis reactions undergoes further cracking and polymerization reactions to produce lighter or heavier hydrocarbons. Several studies have been done on the secondary pyrolysis reactions, which involve the fate of tar and its cracking. Boronson et al. and Liden et al. have reported separately the kinetic parameters of tar cracking derived from wood [17, 44]. Rath and Staudinger also studied the tar cracking kinetics of birch wood particles in a thermo-gravimetric analyser and a coupling of thermo gravimetric analysis (TGA) with a tubular reactor [45]. They showed that the extent of tar cracking is not only dependent on the conditions in the reactor (temperature and residence time) but also on the temperature at which the tar was formed [46]. Most of the kinetic models proposed for tar cracking are based on a single step, first-order reaction. Among different kinetics, the results of Boronson et al. show comparable rates and are the most used. The kinetics of tar cracking has also been studied in another approach. Due to the complexity of the tar, several researchers have studied its cracking and decomposition reactions using a model-biomass–tar compound, such as phenol, toluene, naphthalene, 1-methylnaphthalene, and so on. In most of the proposed kinetics, a first-order reaction for tar cracking was used.

10.4 Catalytic Gasification

The use of a catalyst for gasification is not essential, but it can increase gasification efficiency by reducing tar content or other unpleasant products, such as methane. The application of a catalyst promotes tar cracking at lower temperatures or promotes a steam-reforming reaction, which is a reaction between methane and steam in the temperature range of 700 °C–1,100 °C to produce syngas. The catalyst can be used directly in the gasifier or the secondary reactor downstream of the gasifier [47, 48]. There are different criteria for developing or choosing a proper catalyst, such as being inexpensive, effective, and resistant to attrition, carbon fouling, and sintering. Catalysts used in tar cracking can be classified into three main groups: alkali metals, non-metallic oxides, and supported metallic oxides.

10.4.1 Alkali Metals

Alkali metals, such as sodium and potassium, can promote a tar cracking reaction. Catalysts, such as potassium carbonate and sodium carbonate, are effective in methane production and are available in most biomass ashes. Potassium, however, is well-known for agglomeration in fluidized beds. Studies on the effects of inorganic salts ($MgC1_2$, NaC1, $FeSO_4$, and $ZnC1_2$) on the pyrolysis of cellulose have shown that $MgCl_2$ does not change the overall pyrolysis but has some slight effects on gas production. For the other tested catalysts (NaC1, $FeSO_4$, and $ZnC1_2$), an increase in char production was reported [49].

10.4.2 Non-metallic Oxides

Calcined dolomite is the most popular and most investigated material as a tar cracking catalyst. Dolomite is a calcium magnesium ore with a general chemical formula $CaMg(CO_3)_2$. This catalyst is relatively inexpensive, abundant, and disposable. Aznar, Corella and their research groups, in several publications, have investigated the effect of the in-bed use of dolomite, which can decrease the tar level from 6.5 %wt to 1.3 %wt [50]. The addition of 3–10 % calcined dolomite to biomass feed decreases the tar level by 40 % and improves gas quality significantly [51, 52]. Although dolomite has proved to be effective in terms of tar reduction, it has some critical limitations. Dolomite in its naturally occurring form is not very active in tar cracking, and it needs to be calcined. Calcination of dolomite involves its decomposition and the elimination of CO_2 to form the MgO-CaO complex. Calcination reduces the surface area of the dolomite catalyst, and makes it more friable resulting in severe catalyst attrition and fine-particle production. While using dolomite in a fluidized bed, dust entrainment due to the eroding of soft dolomite particles necessitates the continuous feeding of dolomite into the reactor by mixing it with biomass fuel [51]. This requires a major gas-cleaning operation.

Another popular catalyst in this group is olivine, which could be an alternative for dolomite. Olivine is a mineral, which contains magnesium, iron oxide, and silica. In terms of attrition, olivine has certain advantages over dolomite. However, Corella et al reported that dolomite was 1.4 times more active than olivine in biomass gasification with air, but dolomite generated $\sim 4-6$ times more particulates in the gasification gas than olivine [53]. Nickel has also been used with an olivine support, which led to improved catalytic activity compared to unsupported olivine catalysts [54, 55].

10.4.3 Supported Metallic Oxides

Popular catalysts in this group are Ni-based catalysts. A wide variety of Ni-based steam reforming catalysts are commercially available, and they are widely applied in the petrochemical industry. The literature contains numerous studies reporting the use of commercial Ni-based catalysts for tar cracking, which has been shown to be very effective in increasing synthesis gas yield. However, the use of the Ni catalyst in the gasifier is limited due to its fast deactivation caused by coke, chlorine, and alkali metals that may be present in the gasifier (from biomass ash). So far, the use of a nickel catalyst as an additive to the gasifier has had little success.

All these catalysts, when used in-situ, are not promising due to the combination of coking and friability. Using them in secondary beds is more effective. The duration of most-reported catalyst tests has been quite short, especially considering the long activity requirements for expensive catalysts, such as Ni, to be economical. Although downstream gas cleaning methods are reported to be very effective in tar reduction; catalyst deactivation due to impurities in the gas outlet of the gasifier makes catalytic tar cracking economically unfeasible.

10.5 Product Gas Cleanup and Conditioning

The raw products of biomass gasification contain contaminants, including particles, organic impurities (tar) alkali metals, chlorine, nitrogen, and sulfur compounds (such as H_2S, CS_2, COS, AsH_3, PH_3, HCl, NH_3, and HCN). These contaminations can block the downstream units, such as gas coolers and engines, and also interfere with the catalyst used in the production of synthetic fuels. Therefore, they have to be completely removed or significantly reduced before utilizing the gas depending on the application of interest. Also, the purpose of the conditioning system is to adjust the components to the appropriate ratio. Depending on the type of feedstock, its composition, and the type of gasification product application, there are different types of gas cleaning and conditioning that can be categorized as physical cleaning, such as cyclone, filters, and wet scrubbers' application, or chemical cleaning, such as catalytic cracking, thermal reforming, shift hydrolysis, and hydrogenation.

10.5.1 Particulate Removal Technologies

Particulate impurities in the product gas typically originate from ash, dust, carry-over bed materials, and unconverted char. The particulates can cause corrosion and plugging in the downstream process equipment. The most commonly used techniques for particulate removal are cyclones for the initial cleaning of larger particles, barrier filters (low and high temperature operations), electrostatic filters (ESP), wet scrubbers, and alkali salts. The application of the proper removal technique depends on the concentration of impurities, particle size distribution, and the particulate tolerance of the downstream application.

10.5.1.1 Barrier Filter

Barrier filters work by presenting a physical barrier in the path of tar and particulates while allowing the clean gas to pass through. Their surface can be coated with appropriate catalytic agents to facilitate tar cracking [55]. There are two types of filters: candle and fabric.

Candle filters are porous, ceramic, or metallic and can work at temperatures as high as 900 °C. The porosity of the material is chosen so that the finest particles do not pass through. Particles failing to pass through the filter barrier deposit on the wall and form a layer of solids called a “filter cake”. Candle filters have been shown to fail within a short period of operation, which makes them economically undesirable [56, 57]. The main reasons for filter failure in the case of gasification are as follows: (1) thermal stress or shock due to char combustion on the filter surface; and (2) dust and ash deposition between the candles, which increases the pressure drop over the filter. To improve the lifetime of traditional candle filters, impurities, such as alkalis, chlorine, and sulfur, can be removed by sorbents prior to filter application, which can reduce the risk of weakening due to high-temperature corrosion [58]. Fixed beds with sorbents, such as bentonites or bauxites, can be used to remove alkalis, and CaO sorbents can be used to remove sulfur and chlorine, as CaS and $CaCl_2$ upstream from the particulate candle filter.

Fabric filters are made of woven fabric and, unlike candle filters, can operate only in lower temperatures (<350 °C). The condensation of tar on the fabric is a major problem if the gas is cooled excessively.

10.5.1.2 Wet Scrubber

In this method, water is sprayed on the gas, which makes the particles and tars collide, creating large droplets and separate from the gas stream by using cyclones. The tar liquid can be re-injected into the gasifier, and water may be regenerated by stripping the tar away. This method produces a large amount of waste water with a high organic content, removes a large fraction of the carbon and hydrogen stored in tars, and also reduces the gas temperature to near ambient temperatures, which results in a loss of thermal efficiency.

There are some commercial methods of wet scrubbing available, such as OLGA and TARWTC technologies, which use oil as a scrubbing liquid [59, 43]. The oil with separated tars can be recirculated to the gasifier so the energy in tar can be recovered. In this method, however, cooling the gas prior to cleaning is still required.

10.5.1.3 Alkali Remover

Compared to fossil fuels, biomass has a high concentration of alkali salts, and their removal from the product gas is a very important step in biomass gasification. Alkali salts will condense below 600 °C, which causes serious corrosion problems. If the temperature of the gas decreases below 600 °C, the alkali salts condense and can be separated in a cyclone or filters. However, in some applications, gas cannot be cooled so alumosilicates, such as bauxite, kaolinite, bentonite, and naturally occurring zeolite, can be used for alkali removal at temperatures up to 700 °C [59].

10.5.1.4 Electrostatic Precipitators

Electrostatic precipitators (ESP) are used to remove fine solids and liquid droplets from gas stream; however, they are not very efficient in terms of tar removal at high temperature. In order to have an efficient tar removal, gas stream should be quenched before ESP. In wet ESP, gas is ionised upon passing between high voltage electrodes and a grounded electrode. The produced ions attach themselves to dust particles or tar and water droplets. The charged particles and droplets are attracted to the grounded electrode, flowing to the bottom of the ESP where they are collected.

10.5.2 Tar Removal

Tars in the product gas can be tolerated in some systems where the gas is used as a fuel in applications, such as burners. However, in most of applications, tars in the raw product gases, even at low concentrations, can create major handling and disposal problems. Two basic approaches have been used to remove tars from product gas streams: (1) physical removal technologies similar to those used for particulate removal, such as wet scrubbers, ESP; and 2) catalytic and thermal tar-reduction methods where tars are converted to permanent gases. The catalytic approaches can potentially destroy tars in either vaporized or condensed state. The second approach is discussed below.

10.5.2.1 Thermal Cracking

By increasing the gasifier temperature all organic compounds will crack to smaller hydrocarbons (∼1,200 °C). Oxygen or air can be added to the gasifier to allow partial combustion of the tar to raise its temperature. Using electrical arc plasma for tar cracking is another option. It is a simple technique but it produces gas with lower energy content.

10.5.2.2 Catalytic Cracking

This technique can be applied in the gasifier or in a secondary reactor. The gasifier is commercially used in many plants for the removal of undesired elements from product gas. This method is explained in more detail in Sect. 4. For most syngas applications, the optimization of operating conditions, catalytic gasifier material or additives combined with secondary hot gas cleaning (catalytic cracking) are the most preferred methods.

10.5.3 Inorganic Impurities

Inorganic compounds, such as Cl and S-containing material, HCN, COS, and ammonia, can be removed by means of physical and chemical washing techniques. Removal of ammonia from biomass is necessary in many situations since they are converted to NO_x when gas is burned. Ammonia can be removed by catalytic destruction using catalysts similar to those used for tar cracking and also by wet scrubbing where low temperature product gases are acceptable. Catalysts, such as dolomite, nickel-based steam reforming catalysts, and iron-based catalysts, have been used for ammonia removal with $> 99\ \%$ efficiency. Catalytic removal is economically an attractive option since it has the potential to remove tar and ammonia from product gas while keeping its heat [60].

In systems where product gas is first cooled, ammonia can be removed by wet scrubbing. The ammonia recovered from the scrubber is reinjected into the gasifier to reduce ammonia production through equilibrium.

H_2S can be removed by different sorptions, such as metal oxides, Cu- and Ca-based sorbents. For example, the Selexol process uses dimethyl ethers of polyethylene glycol and the Rectisol process employs methanol as a solvent to remove H_2S and COS and simultaneously remove CO_2 from syngas [61].

10.5.4 CO_2 Removal

Carbon dioxide can be removed from syngas by chemical and physical absorption with a washing liquid or by adsorption with solid absorption. The choice for chemical or physical absorption (or a combination of both) depends on the partial pressure in the gas. For chemical absorption in commercial processes substituted amines are used, while solvents, like methanol, polyethylene glycol, and dimethyl ether, are used for physical absorption. The CO_2 concentration can be removed to approximately 0.1 vol% by these processes. When the syngas contains significant concentrations of other gases besides H_2 and CO_2, adsorption on solid materials, such as silica gel, active carbon, zeolites, and molecular sieves, is preferred.

As discussed earlier, the produced syngas often contains high amounts of problematic impurities, such as sulfur, chlorine, and alkalis. The gasification process has several cleaning units and its total efficiency depends on the heat management of the various steps. One of the most important challenges for an efficient gas cleaning process is developing a hot gas cleaning technology, which works at or close to the gasifier temperature. These techniques include the development of novel particulate removal techniques, an improved catalyst for tar cracking to produce a tar- and particulate-free product gas and a higher degree of process integration. For example,

Table 10.3 Characteristics of different categories of the gasification process

Application criteria	Updraft	Downdraft	Cross-draft	Fluidized bed	Entrained flow
Fuel moisture (%)	60 max	25 max	10–20	20–30	35
Ash-dry basis (%)	25 max	6 max	05–1.0		Slurry feed: 20 max dry ash: 40
Ash melting temp (C)	>1000	>1250	–		
Feedstock size (mm)	5–100	20–100	5–20	6–10	$< 100\ \mu$m
Application range (MW h)	2–3	1–2	–	< 25	< 50
Gas exit temp (C)	200–400	700	1,250	900–1,050	1,250–1,000
Tar (g/N m^3)	30–150	0.015–3.0	0.01–0.1	1–3	–
Gas LHV (MJ/N m^3)	5–6	4.5–5.0	4.0–4.5	–	–
Hot-gas efficiency (%)	90–95	85–90	75–90	–	–
Turndown ration	5–10	3–4	2–3	–	–

References: [43, 62]

one possible way to increase the efficiency of hot gas cleaning and also reduce the cost is to decrease the number of gas cleaning stages by combining different physical and chemical processes in the same equipment, such as catalytic tar cracking in a particular barrier filter. This was first proposed for combustion applications [62], but further applied to the gasification process by many research groups, such as the deposition of the Ni/MgO catalyst onto the pore walls in α-alumina in a candle [63] and a catalytically active fixed bed in a cylindrical catalytic filter element [64]. Still, there is continuous research and development being done to improve particulate filtration, various sorbents and associated equipment to achieve a high efficiency of gas cleaning, especially at high temperatures.

10.6 Types of Gasifiers

The chemical composition of the gasification product strongly depends on the type of gasifier. Different reactors have been used to perform the gasification process. The different types of reactors can be categorized based on the specifics of the solid transportation in the reactor or the means by which the gasifying agent is introduced to them. The main characteristics, advantages, and limitations of the most widely used gasifiers are summarized in Table 10.3.

10.6.1 Fixed Bed Gasifier

This type of reactor consists of a cylindrical reactor with a fixed bed of solid fuel. The gasifying agent is injected upward or downward through the reactor. These simple reactors can operate at high carbon conversion, for a long solid residence time, at

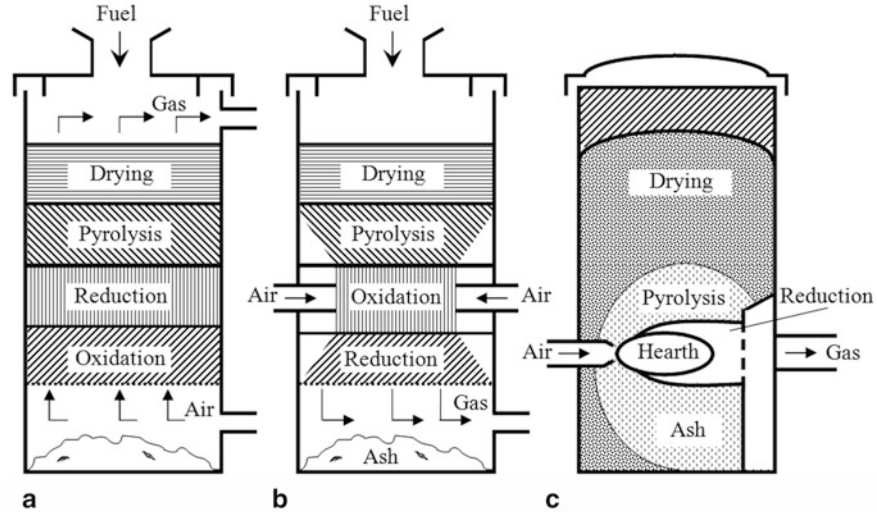


Fig. 10.1 Fixed bed gasifiers: (**a**) updraft, (**b**) downdraft, (**c**) cross-draft

low gas velocity and they are suitable for small scale applications, that is, <10 MW [65]. Fixed bed gasifiers are classified into three groups according to the way the biomass and gasifying agent enter the reactor.

10.6.1.1 Updraft Gasifier

Updraft gasifiers are the oldest and simplest type of gasifier. In these reactors, the gasifying gas travels upward while the solid fuels move downward as shown in Fig. 10.1a. The major advantage of this type of gasifier is its simple structure and design, low capital cost, and high char burn-out, which leads to low gas exit temperatures and high equipment efficiency, as well as the possibility to process feedstock of various shapes [66].

On the other hand, poor heat and mass transfer can increase the risk of "channelling" in the equipment, which may lead to an oxygen breakthrough and rapid gas-phase combustion reactions (and, possibly, an explosion). Fuels that are prone to agglomeration during gasification are not suitable for these types of reactors due to poor heat and mass transfer. However, high-ash, high-moisture or low-volatile feedstocks are suitable fuels for updraft gasifiers. Also, there are problems associated with high tar production that require gas cleaning operations. This is of minor importance, though, if the gas is used for direct heat applications, where the tar simply can be burnt. Nonetheless, this is not recommended for engine applications.

10.6.1.2 Downdraft Gasifier

The problem of tar entrainment in the gas stream had been solved by designing downdraft gasifiers where the gasifying agent enters from the top and the gaseous products leave the reactor through a bed of hot ash at the bottom. A schematic of this reactor is shown in Fig. 10.1b. The main advantage of downdraft gasifiers lies in the *possibility* of producing a tar-free gas from high volatile fuels which will be suitable for engine applications. This is due to the fact that most of the tar is cracked when passing through the hot ash before exiting the reactor. A major drawback of this type of gasifier is its inability to operate with a wide range of fuels. In particular, fluffy, low density materials can cause flow problems, like an excessive pressure drop, requiring the solid fuel to be pelletized or briquetted before use. Downdraft gasifiers also suffer from slagging when operating with fuels characterized by high ash content. Compared to updraft gasifiers, downdraft systems show lower efficiencies resulting from a lack of internal heat exchange as well as the LHV of the gas.

10.6.1.3 Cross-draft Gasifier

This type of gasifier is suitable for low ash fuels. Unlike downdraft and updraft types, it releases the product from its sides. Air at high velocity enters the gasifier through a nozzle at a certain height above the grate creating a very high temperature zone. The product gas exits from the opposite sides of the gasifier. Start-up time is much faster (5–10 min) compared to other moving bed gasifiers, which improves the response to load changes. Due to relatively high temperature zones on a cross-draft gasifier, the product gas is low in tar, high in carbon monoxide, and low in hydrogen and methane.

10.6.2 Fluidized Bed Gasifier

Fluidized bed reactors have been used extensively for coal gasification. Fluidized bed gasifiers are characterized by excellent heat and mass transfer, which facilitates the control of the bed temperature. Furthermore, this allows the use of a wide variety of fuels, such as fluffy and fine grained materials without the need of pre-treatment. However, problems with solid feeding and fly-ash sintering in the gas channels can occur with some biomass fuels.

There are two major categories of fluidized beds for biomass gasification: bubbling (BFB) and circulation fluidized beds (CFB). These two types of gasifiers are characterized by significantly different gas and solids hydrodynamics. CFBs are operated with a higher gas velocity (3–5 m/s) compared to BFB (0.4–1 m/s). In CFBs, the solid particles are entrained along a tall tubular section (called a riser), which allows long gas and solid residence times. CFB gasifiers at atmospheric pressure have proven very reliable with a variety of feedstock and are relatively easy to scale up from a few MWh up to 100 MW h [67].

The family of fluidized bed reactors include other relatively new concepts for gasifiers: chemical looping, dual gasifier, and an internally circulating fluidized bed. The main motivation driving the development of these reactors is to reduce the syngas dilution in nitrogen or carbon dioxide. In chemical looping gasification, a solid oxygen carrier is circulated continuously between two fluidized bed reactors: (1) a biomass fluidized bed gasifier and (2) a fluidized bed to oxidize the oxygen carrier. In the gasifier, the oxygen-carrier releases the oxygen for the gasification reactions before being entrained back to the second fluidized bed where it is re-oxidized [68]. The concept of circulating solids between two fluidized beds has also been extensively studied for CO_2 capture [69]. There is currently an operating industrial plant in Gussing (Austria), which consists of one circulating fluidized bed combustor and a bubbling fluidized bed gasifier. This system has, however, its own drawbacks. For example, the amount of char combustion in the gasifier may not be sufficient to provide the required heat for endothermic reactions. Co-firing may therefore be necessary [70].

10.6.3 Entrained-Flow Gasifier

Entrained flow gasifiers consist of a co-current plug flow reactor and have been extensively studied and used for coal gasification. The gas and particle residence times in the reactor are very short (a few seconds), which requires very small size feedstock (100 μm) and very high temperature (>1,000 °C) to maximize conversion. There are two types of entrained flow gasifiers: slagging and non-slagging. In the slagging gasifier, the ash melts in the gasifier, flows down the walls of the reactor and finally leaves the reactor as a liquid slag. This type of entrained flow gasifier is preferred for biomass. In a non-slagging gasifier, the walls are free of slag, which is suitable for feedstock with low ash content [71]. Some of the advantages of entrained flow gasifiers are low tar and methane content, high carbon conversion, and ash existing as slag. Furthermore, the reactor can be operated, with a wide variety of feedstock at high pressure and temperature. Due to some problems associated with biomass molten ash and the use of very fine biomass particles, however, the use of an entrained flow biomass gasifier has been rather limited. One example of an entrained flow gasifier application for biomass is the Choren process with a maximum capacity of 45 MW h and using wood as feedstock [72].

10.6.4 Plasma Gasifier

Plasma gasifiers use a plasma gun to create an intense electric arc between two electrodes. The temperature of the arc can reach extremely high (>13,000 °C). Biomass, on the other hand, is fed at lower temperatures (2,700–4,500 °C), but still sufficiently high to crack heavy hydrocarbons. Due to its high operating temperature, the plasma

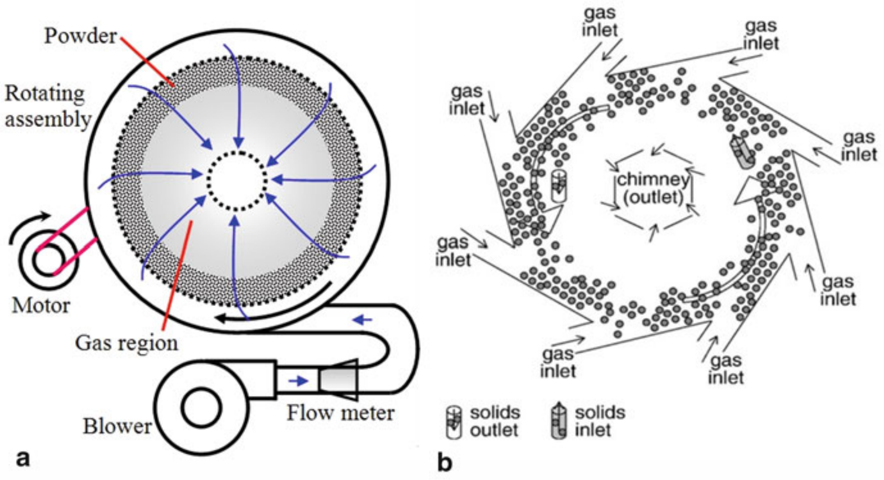


Fig. 10.2 Sketch of a (a) conventional rotating fluidized bed and (b) novel rotating fluidized bed. (Reprinted from ref. [74], Copyright 2008, with permission from Elsevier)

gasifier can crack harmful products, such as furan and dioxin, making it suitable for MSW and other types of waste products.

10.6.5 Rotating Fluidized Bed Gasifier

As previously discussed, heat and mass transfer play an important role in the gasification process. As such, fluidized beds are advantageously characterized by high heat and mass transfer rates that will result in temperature homogeneity and the rapid mixing of particulate materials. Heat and mass transfer are maximized by increasing the gas fluidization velocity, but the gas velocity cannot be indefinitely increased. With increasing superficial gas velocity the solid hold up in the bed region decreases causing a short solid residence time and a low conversion or reactor volume increase. To overcome these limitations of conventional fluidized bed gasifiers, the concept of a rotating fluidized bed (RFB) has been introduced. RFB reactors were first patented by Horgan and Morrison in 1979 for a coal combustion application in a centrifugal fluidized bed [73]. RFB consists of a cylindrical gas distributor chamber rotating around its axis (shown in Fig. 10.2). The rotating motion of the cylinder is transferred to the particles via fraction and gas is injected inward through the gas distributor. The particles are fluidized uniformly under the action of two opposite forces: the radially inward drag force exerted by the injected gas and the radially outward centrifugal force. The minimum fluidization velocity increases with increasing the reactor rotation speeds (rising centrifugal force magnitude). The magnitude of the forces, which can be much higher than gravity, depends on the operating conditions: solid rotating velocity and gas injection velocity.

The rotating motion of RFBs may cause difficulties in design and operation, like severe vibrations of the reactor during operation. To overcome these difficulties, a new concept of a rotating fluidized bed has been proposed where the geometry of the reactor is fixed and the fluidizing gas is injected tangentially via multiple gas inlet slots at the fluidization chamber wall. As a result, the tangential drag force will induce the solid particles into a rotating motion as well as produce a radially outward centrifugal force [74]. The RFB reactor can operate at much higher gas velocities and solid hold-up compared to the fluidized bed. Due to high attrition the novel RFB reactor is suitable for processes where solid is a reactant, like biomass gasification [75].

As discussed above there are several options when choosing and designing a gasifier. The choice of one type of gasifier over another is, however, determined by the type of fuel, its size, the moisture content, the physical limitations of the reactor, its production capacity and the final use of the product gas since one type is not necessarily suitable for the full range of capacities. The different gasifier characteristics are summarized in Table 10.3.

10.7 Gasifier Reaction Modeling

Gasifier performance could be expressed in terms of gasification efficiency and product quality, such as heating value and the amount of desired product gas. Mathematical modeling and simulation of the gasification process provides qualitative information on the gasifier performance, such as the effect of feedstock, design parameters, and operating conditions of the process even though it is not very accurate. A mathematical model or simulation is, however, useless if it cannot reproduce experimental data with acceptable deviation [14]. Gasifier models could be classified into the following groups: thermodynamic equilibrium, kinetic, artificial neural network and computational fluid dynamics (CFD).

10.7.1 Equilibrium Models

The equilibrium model predicts the maximum yield when the reactants are in contact for an infinite time without taking into account the reactor type and size [76]. In reality, the products leave the reactor before having the opportunity to reach equilibrium so this type of model only provides the ideal yield. For practical applications, therefore, the use of the kinetic model is more realistic. At higher temperatures ($>$1,500 K), however, the use of the equilibrium model is more effective. There are two types of equilibrium modeling approaches: (1) stoichiometric or the use of the equilibrium constant; (2) non-stoichiometric or the minimization of Gibbs free energy method. In the stoichiometric model, all the chemical reactions and species involved are considered. For a known reaction mechanism this method predicts the maximum yield of all the products and the possible limiting behavior of the reactor. In the

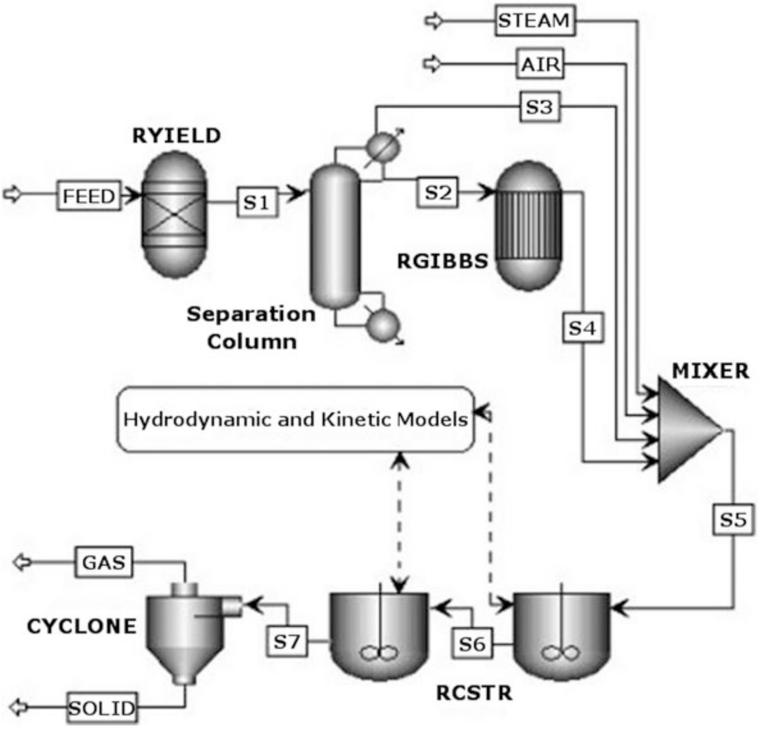


Fig. 10.3 Comprehensive simulation diagram for the fluidized bed gasification process. (Reprinted from Ref. [83], Copyright 2008, with permission from Elsevier)

non-stoichiometric method, however, no knowledge of the reaction mechanism is required. This method is based on the minimization of total Gibbs energy with only the input of feed composition and is suitable for fuels, like biomass, although the chemical reaction mechanism is not very clear.

Also process simulators such as Aspen Plus, Simulink [77] and, Cycle Tempo [78] have been used to evaluate mass and energy flows and to perform economic and environmental evaluations. Gasification process simulation were done by considering thermodynamic equilibrium by minimizing the Gibbs free energy [77, 79]. Mathieu et al. modeled wood gasification in a fluidized bed using Aspen Plus [80]. The model was based on the minimization of the Gibbs free energy and the process was uncoupled in pyrolysis, combustion, Boudouard reaction and gasification. Other simulations were proposed based on using two equilibrium reactors in series with a selective by-pass over the first one [80] or by breaking up biomass into its constituting elements (C, H, N, O, S, Cl, ash, and moisture) dealing with them separately [81–84]. Mitta et al. modeled a fluidized-bed tire gasification plant with air and steam using Aspen Plus [85]. Their gasification model was divided into three different stages: drying, devolatilization-pyrolysis and gasification-combustion. Nikoo and Mahinpey developed a model capable of predicting the performance of an atmospheric fluidized-bed gasifier [83]. They used both built-in Aspen Plus reactor models and external FORTRAN subroutines for hydrodynamics and kinetics to simulate the gasification process. Other authors have worked with Aspen Plus to model the gasification process for coal and biomass. Yan and Rudolph developed a model for a compartmented fluidised-bed coal gasifier process [86], Sudiro et al. modeled the gasification process to obtain synthetic natural gas from petcoke [87]. Abdelouahed proposed a compressive model for dual fluidized bed gasifier modeling with ASPEN Plus [88]. A comprehensive review on Biomass gasification simulation also provided by Puig-Arnavat et al. [90] (Fig. 10.3)

10.7.2 Kinetic Models

Gas composition exiting a gasifier often varies from the composition predicted by equilibrium models [76]. This is caused by the fact that products exit from the reactor before reaching an equilibrium state and thus demonstrates the need for kinetic models to simulate gasifier behavior. Gasification reactions are divided into three categories: drying, devolatilization, and gasification. The time taken for drying and devolatilization is much faster than gasification of char. Some models assume the first two steps to be instantaneous and that the rate of char gasification controls the overall process [89, 90].

Kinetic models provide information on the progress of the reaction by taking into account the reactor type, size, and its hydrodynamics. In the kinetic model, the reaction kinetic is solved simultaneously with bed hydrodynamics, mass and energy balance to achieve the gas, and tar and char yield at specific operating conditions. Unlike other models, the kinetic model is sensitive to the gas-solid mixing and the flow pattern in the gasifier. Based on the process, this type of model can be divided into three groups: (1) fluidized bed; (2) fixed bed; and (3) entrained flow.

10.7.2.1 Fluidized Bed Kinetic Model

The kinetic model of the fluidized bed gasifier consists of reactor hydrodynamics, which define the transport phenomena of the gasification medium through the system and solid mixing behavior. There are several versions of fluidized bed hydrodynamic models [91–93]:

1. The two-phase model in a bubbling fluidized bed, which considers bubble and emulsion phases.
2. The three-phase model in a bubbling fluidized bed consists of bubbling, cloud, and emulsion phases.
3. The core-annulus model for circulating fluidized beds where the core is the upward flow of gas and solid in the center and the annulus is the downward flow of gas and solid close to the wall.

4. The compartment models in which the fluidized bed is divided into slices or horizontal sections.

These types of fluidized bed models avoid the complexity of gas-solid dynamics but still keep the fluid-dynamic effects by considering different regions and phases throughout the reactor, which are described by semi-empirical correlations [91, 92, 93, 94 and 95].

Gas flow through the bed can be modeled as follows:

1. Bubble phase as plug flow and emulsion phase as ideally mixed gas.
2. Both phases as ideally mixed gases.
3. Both phases as plug flow with mass transfer between two phases.
4. Upward gas in the core as plug flow and solid backflow in the annulus [95].

There are three ways to describe conversion models for single char particles:

1. Shrinking core model;
2. Shrinking particle model; and
3. Uniform conversion model [96, 97].

Shrinking core and shrinking particle models are both surface reaction models where the fast reaction takes place as soon as the reactant gas reaches the external surface of the particle. In the shrinking particle model, however, the ash peels off instantaneously and the particle shrinks during reaction. In the shrinking core model, the particle size stays constant since the ash remains attached to the particle and becomes an additional heat and mass resistance. In the uniform conversion model the reaction takes place all over the char particle uniformly.

Different types of fluidized bed modeling have been applied for coal and biomass gasifiers [90, 98–102]. The following section presents essential equations for a one-dimensional steady-state model of a bubbling fluidized bed gasifier. The fluidized bed is divided into two regions, a dense zone and a free board. The gas flow in the dense part consists of bubble and emulsion phases, which deals with drying, pyrolysis, and gasification of biomass. The freeboard is free of solid particles and only gas phase reactions continue from the bed. The mass balance for the emulsion and bubble phases can be expressed as (10.1) and (10.2):

Emulsion phase:

$$\begin{aligned}&-(1-\delta_b)\varepsilon_{mf}\tfrac{d}{dz}(C_{ie}u_e)-K_{be}(C_{ib}-C_{ie})+(1-\delta_b)(1-\varepsilon_{mf})\Sigma_{g-s}R_i+\\&(1-\delta_b)\varepsilon_{mf}\Sigma_{g-g}R_i=0\end{aligned} \tag{10.1}$$

Bubble phase:

$$\begin{aligned}&-\delta_b\frac{d}{dz}(C_{ib}u_b)+K_{be}(C_{ib}-C_{ie})+\gamma_b\delta_b\Sigma_{g-s}R_i+\\&(1-\gamma_b)\delta_b\Sigma_{g-g}R_i=0\end{aligned} \tag{10.2}$$

The boundary conditions for the above equations are defined in the feeding zone, which is the gas composition, predicted using the pyrolysis kinetics.

For solid hydrodynamics, a concurrent back mixing model is considered [95]. Based on the CCBM, (10.3) could be written for the char particles.

Char balance in the ascending phase:

$$F_{as,0}\frac{dX_{as}}{dz} + K_w(C_{ds,c} - C_{as,c})Af_{as} + Af_{as}\Sigma_{g-s}R_i = 0 \tag{10.3}$$

Char balance in the descending phase:

$$-F_{ds,0}\frac{dX_{ds}}{dz} + K_w(C_{as,c} - C_{ds,c})Af_{as} + A(1 - f_{as})\Sigma_{g\text{-}s}R_i = 0 \tag{10.4}$$

The bubble and emulsion equations, which give the gas concentration profile in the bed, and the char balance equation, which provides the char conversion profile in the bed, will be solved simultaneously for all gas species to obtain produced gas compositions and yields in the bed.

Based on this assumption there won't be any solid in the freeboard and it will be considered as a plug flow reactor. The mass balance for each gas species in this region can be written as (10.5):

$$\frac{d(u_g C_{i,g})}{dz} = \sum\nolimits_{g-g} R_i \tag{10.5}$$

10.7.2.2 Updraft Kinetic Model

The major assumptions regarding the moving bed (updraft gasifier) model are as follows:

- There is no temperature or concentration distribution radially.
- The solid hydrodynamic is considered as a plug flow flowing downward.
- The gas flows upward as a plug flow.
- The mass transfer between two phases takes place by diffusion [14].

The mass balance equation of jth-gas species can be written as (10.6):

$$u_g\frac{d\rho_{g,j}}{dz} = D_{g,j}\frac{d^2\rho_{g,j}}{dz^2} + R_{m,j} \tag{10.6}$$

Also, the energy balance of the gasifier in the z direction is expressed as follows:

$$\rho_g C_g u_g\frac{dT}{dz} = \lambda g\frac{d^2T}{dz^2} + Q_{\text{gasification}} + Q_{\text{conv}} + Q_{\text{rad}} + Q_{\text{mass}} \tag{10.7}$$

These equations will be solved simultaneously with the appropriate kinetics discussed in section 3.

10.7.2.3 Entrained Flow Gasifier

The reactor is considered as a one-dimensional plug flow reactor under steady-state conditions [94]. The gas phase is considered as perfectly mixed radially and the solid particles are distributed uniformly in the radial direction. The mass balance for solid and gas components can be described as follows [103]:

$$\frac{dW}{dL} = -N_v A \sum r_k(T_S, L) \tag{10.8}$$

$$\frac{dF_{g,i}}{dL} = \pm N_v A \sum v_{1k} r_k(T_S, L) \tag{10.9}$$

10.7.3 CFD Models

CFD modeling solves a set of equations for the conservation of mass, momentum, and energy simultaneously to give the gasifier temperature, the product concentration, and the hydrodynamic parameters at different locations. Due to the complexity of the gasification process, however, there are not many CFD models available for this process and most of them must use fitting parameters and major assumptions for areas where accurate information is not available. Most of the CFD models are for coal gasification and combustion in entrained flow reactors since gas–solid flow is less complex compared to fluidized bed reactors [104] and [105]. A typical CFD model for gasification consists of a set of sub-models for different reactions and phenomena, such as drying biomass particles, devolatilization (pyrolysis), secondary pyrolysis, and char oxidation [106]. There are also other sophisticated subroutines for the destruction of solid fuels during gasification and combustion, which could be coupled with transport phenomena of the gasifier [107]. Due, however, to considerable computational times for CFD models, particularly when chemical reactions are involved, this type of modeling is not very common for fluidized bed gasifiers.

10.7.4 Neural Network Models

Neural network models basically rely on a large number of experimental data [108, 109]. This model connects the input and output of a process unit with less knowledge of the system phenomena compared to the equilibrium and kinetic approaches. Guo et al. developed a neural network model for biomass gasification in a fluidized bed and emphasized its success and applicability for this process.

Symbols and Nomenclature

A = Cross-sectional area of the gasifier (m^2)
C = Molar concentration (mol/m^3)
C_p = Specific heat

D = Diffusion coefficient (m^2/s)
F = Molar flow rate (mol/s)
$Q_{\text{gasification}}$, Q_{conv}, Q_{rad}, and Q_{mass} = Energy transfer due to gasification, convection, radiation (kW/m^3 of bed)
R = Reaction rate (kg/m^3 s)
X = Char conversion
u = Gas velocity (m/s)
W = Solid flow rate (kg/s)

Subscripts
as = Ascending phase
b = Bubble
be = Bubble-emulsion
c = Char
ds = Descending phase
f = Freeboard
g = Gas phase
i = Gaseous components in the product gas
k = Reaction number
w = Wake

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